

Enthalpy of Fusion of Zirconium

Preliminary Recommendation

The preliminary recommendation for the enthalpy of fusion of zirconium is

$$150 \pm 44 \text{ J/g} = 13.7 \pm 4 \text{ kJ/mol}$$

This value for the enthalpy of fusion is an average of the enthalpy of fusion obtained by Korobenko and Savvatimskii [1] from pulse heating measurements of the enthalpies of the solid and liquid phases at the melting point ($2128 \pm 5 \text{ K}$) and the enthalpy of fusion obtained from magnetic levitation measurements by Katz [2]. It is identical with the recommendation by Gurvich et al. [3]

Uncertainty

The uncertainty in this first recommendation for the enthalpy of fusion of zirconium is $\pm 29\%$, the uncertainty given by Gurvich et al.[3] The large uncertainty reflects the large range in the measured values (138 - 285 J/g) as well as the large range in values recommended in the assessments in the literature (140 to 230 J/g).

Discussion

Table 1 lists the values for the enthalpy of fusion of zirconium recommended in the literature in chronological order. In 1963, Hultgren et al.[4] recommended 225 J/g (20.5 kJ/mol) for the enthalpy of fusion based on estimates using Richard's rule. In 1967, Elyutin et al.[5] recommended 229 J/g (20.9 kJ/mol) based on their three measurements by the method of mixing in a liquid magnesium calorimeter. The values obtained in these experiments are shown in Table 2. In reviewing the data, Korobenko and Savvatimskii [1] comment that the heat of mixing of the liquid zirconium and magnesium were neglected in the analysis of the experimental data. The 7% error reported by Elyutin et al. is the uncertainty in the data analysis. It is the range of data not the total experimental error.

Martynyuk et al. measured the enthalpy of fusion using electrical resistive heating with 20 μsec [15] and 400 μsec pulses. Although, the value 285 J/g with a 15% uncertainty from the faster pulse-heating experiments was reported in a university publication [15], it was not included in the journal papers published by Martynyuk and Tsapkov [16, 17]. Martynyuk and Tsapkov reported a heat of fusion of 236 J/g with a 6% uncertainty from 400 μsec pulse heating experiments. This value, obtained by dynamic methods, was in good agreement with the earlier drop calorimetry value [5] and the calculated enthalpy of fusion [4] and widely accepted. However, Korobenko and Savvatimskii [1] question the accuracy of this measurement because the experimenters did not record an inflection in the resistivity that designates the onset of melting, the luminescence nor the temperature. In addition, Korobenko and Savvatimskii found that heating with long 400 μsec pulses led to sample deformation at the onset of melting due to nonuniform heating.

In his thesis, Bonell estimated the enthalpy of fusion of zirconium as 156 J/g from extrapolation of the enthalpies and heat capacities measured at 2233 -2839 K using magnetic levitation in an adiabatic calorimeter. In 1973, Hultgren et al.[6] gave 185 J/g as an estimate of the enthalpy of fusion of zirconium. This value is considerably lower than their previous estimate and it is not clear whether the data of Bonell were taken into account in this estimate. In the 1976 IAEA special volume on zirconium, Alcock et al. recommended 206 J/g (18.8 kJ/mol) by combining the new estimate of Hultgren [6] with the value recommended by Elyutin et al. from their calorimetry measurements. Although the recommendations of Gerasimov et al. [8] and of Gurvich et al. [3] are consistent with the enthalpy of fusion obtained from measurements by Bonell, Gurvich estimated the uncertainty as 29% based on the inconsistencies in the data. Later assessments rejected Bonell's data. The 1985 JANAF Thermochemical Tables [9] recommended 229 J/g based on their 1979 assessment which included only the measurements of Elyutin et al.[5] and of Martynyuk and Tsapkov [17]. In his thorough review of zirconium properties, Guillermet [10] stated that the enthalpy measurements of Bonell appear to have a systematic error but their slope seems reasonable and may be used to obtain a constant liquid heat capacity. He recommended 230 J/g (21 kJ/mol)

based on the drop-calorimetric data of Elyutin et al.[5] because this value has been supported by measurements by Martynyuk and Tsapkov [16] by a dynamic method. The assessment and recommendations of Guillermet [10] were also recommended by the Scientific Group Thermodata Europe [12] for use in phase diagrams and by Cordfunke and Konings[11].

Although the paper by Korobenko and Savvatimskii [1] cites magnetic-levitation measurements of Kats et al. [2], which confirmed measurements of the enthalpy of the solid at the melting point and showed that the earlier measurements of the liquid enthalpy by Elyutin et al. and by Martynyuk and Tsapkov are inaccurate, the paper by Kats et al. does not exist in the English translation of *Teplofizika Vysokikh Temperatur*. Therefore, it was not readily available to Guillermet.

Because of the inconsistency in the published zirconium enthalpy of fusion data and recommendations, Korobenko and Savvatimskii [1] performed two series of electric current pulsed heating experiments of zirconium at 20 and 100 μsec . They performed no experiments with a longer pulse (400 μsec) because they have found that for longer pulses, the surface tension and electromagnetic forces cause the conductor to deform from the onset of melting, indicating nonuniform heating and making property measurements meaningless. Enthalpy results of the two series of measurements by Korobenko and Savvatimskii [1] and their recommendation from their measurements are shown in Table 2. They made additional measurements to make certain that their results are reliable. Their enthalpy of fusion at the melting point is consistent with the values obtained by magnetic levitation of Bonell [18] and of Kats et al.[2] and is significantly lower than the values obtained by Martynyuk and Tsapkov[16,17]. They comment that the enthalpy of copper near the melting point determined by Martynyuk and Tsapkov[16,17] was high by about 70% and later refuted by subsequent pulsed heating experiments.

Despite the availability of these new data, the enthalpy of fusion given in the most recent version of MATPRO[13] remains 225 J/g, the value recommended in 1981[19]. It was based on a 1968

recommendation by Brassfield [20]. The enthalpy of fusion recommended in the IBRAE database and in their review of liquid properties [21] is 206 J/g, the value recommended in the 1976 IAEA publication by Alcock [7]. In the review of liquid properties by the Russian International Nuclear Safety Center (RINSC) [22], the enthalpy of fusion of 150 J/g, given in the Handbook of the Thermodynamic Properties of Individual Substances by Gurvich et al. [3] was recommended.

The enthalpy of fusion recommended by Gurvich et al. [3], 150 J/g, has been selected for preliminary recommendation. It is the average of the two sets of recent measurements by two different techniques. Katz et al.[2] used magnetic levitation. Korobenko and Savvatimskii used pulse-heating. This group's expertise in pulse-heating measurements on a variety of metals including a careful study of the effects of heating rate on the heat capacity of Zr-Nb alloys provides confidence in their results. Their thorough assessment of the published experimental data and evaluation of the experimental techniques to determine sources of error in the experiments, indicate no difficulty with the measurements by Katz et al.[2]. The large uncertainty, given by Gurvich et al. has been included in the preliminary recommendation for two reasons: (1) an enthalpy of fusion of 230 J/g has been widely accepted in the western scientific community and is used in many existing severe accident analyses as well as in phase-diagram calculations because of lack of knowledge of the Russian measurements; (2) for acceptance with a lower uncertainty publication of pulse-heating measurements in the solid phase (1500-2100 K, where the reliable data of Cezairliyan and Righini [23] are available for comparison) through the melting point and in the liquid phase in a widely available peer-reviewed journal are required.

Because of the disagreements in the available data for the enthalpy of fusion, additional measurements to determine the zirconium enthalpy of fusion and the temperature dependence of the enthalpy and heat capacity of liquid zirconium are expected to begin in 1998 at the United Institute of High Temperature, Russian Academy of Sciences. This preliminary recommendation will be reassessed when results of these measurements are available.

References

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